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**CHEMICAL FACTORS ASSOCIATED WITH
ENVIRONMENTALLY-ASSISTED CRACKING
OF GENERIC GUN SYSTEMS**

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13. ABSTRACT (Maximum 200 words) In the last five years, environmentally-assisted cracking (EAC) has resurfaced as a service life-limiting factor for some gun system designs. In these EAC-affected system designs, mechanical loading factors alone do not appear to explain this loss of service life; chemical factors are also implicated. Using standard interior ballistic and nonideal gas-wall thermochemical analyses, the effect of EAC chemical factors is evaluated for three diverse generic gun systems encompassing the spectrum of gun system types. This study indicates that hydrogen-assisted cracking is the type of EAC responsible for such service life limitation. Results show that these hydrogen-producing and embrittling chemical factors include a major effect due to the addition of lubricants, a minor effect due to pressure oscillations, a subtle effect due to gaseous water-wall reactions, another subtle effect due to wall material choice, and nearly no effect due to gaseous acid-wall reactions.				
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INTRODUCTION

In 1874, Johnson and Thomson (ref 1) showed that only acids (hydrochloric, sulphuric) evolving hydrogen by their action on iron and steel embrittle these materials. This explains nitric acid's limited embrittlement of iron and steel, since its action on these materials does not readily liberate hydrogen.

In 1959, Troiano (ref 2) outlined his theory for hydrogen-assisted cracking (HAC), which has stood the test of time and is still accepted today. He stated that HAC causes crack formation and growth in the presence of sufficient loading and in the absence of a known chemical reaction mechanism. Notable variables associated with HAC include time, stress level and state, microstructure, environment, pressure, temperature, hydrogen concentration, bulk metal physical and mechanical properties, surface conditions, diffusion rates, hydrogen source distance, and moving crack front dynamics, all of which share a variety of complex interrelationships. For HAC of steels, Troiano stated that the cohesive strength of the lattice is lowered by the segregation of uncondensed interstitial hydrogen in the lattice at the region near the tip of the dislocation array. He stated that surface adsorption of precipitated hydrogen gas on an unoxidized crack or imperfect lattice surface lowers the surface energy necessary for extension of the crack. He further stated that the electrons of the hydrogen atoms in solution in these transition metals will enter the *d* bands of the metallic cores. The repulsive forces determining the interatomic distance of these transition metals are due to the overlap of the *d* bands. Increased electron concentration of the *d* bands produces an increase in repulsive forces between the metallic cores, which, in turn, translates to a decrease in the cohesive strength of the lattice.

In the last five years, environmentally-assisted cracking (EAC) has resurfaced as a service life-limiting factor for some gun system designs. In these EAC-affected system designs, mechanical loading factors alone do not appear to explain this loss of service life; chemical factors that focus on HAC are also implicated (ref 3).

PROCEDURE

Using standard interior ballistic (NOVA, LPOSC) and nonideal gas-wall thermochemical (BLAKE, C/CET) code analyses (refs 4-7), the effect of EAC chemical factors is evaluated for three diverse generic gun systems encompassing the spectrum of gun system types. An LSENS chemical kinetics code analysis (ref 8) was used to show that although the entire system is not always at equilibrium, near equilibrium conditions exist at any given location and can be treated as an ideal stage, since the chemical reactions at that process point come to an apparent equilibrium many orders of magnitude faster than the "constant" pressure and temperature oscillation frequencies (kilohertz to tens of kilohertz frequency range).

These gun systems include:

- A generic solid propellant tank (SPT)
- A generic solid propellant howitzer (SPH)
- A generic liquid propellant howitzer (LPH)

In addition, three other related system cases were considered with their typical lubricants including:

- A generic lubricated solid propellant tank (SPT,L)
- A generic lubricated solid propellant howitzer (SPH,L)
- A generic lubricated liquid propellant howitzer (LPH,L)

The appended L signifies the addition of a very conservative quantity and type of lubricant associated with each gun system. For all three gun systems, lubricant is added for system storage and becomes part of the combustion products of the next shot fired. For the LPH gun system, significant lubricant is required for the operation of firing each shot and becomes part of the combustion products of each shot fired. Of the six system cases, the only one that does not exist in reality is the LPH system case since significant lubricant is needed to fire this system. The LPH system case was added for comparison and illustrates the enormous possible decreases in embrittling chemical factors if the lubricant dilemma could be solved.

RESULTS AND DISCUSSION

HAC is the type of EAC implicated for service life limitation of some gun system designs (ref 3). Possible hydrogen-producing and embrittling chemical factors (CFs) include addition of lubricants, pressure oscillations, gaseous water-wall reactions, wall material choice, and gaseous acid-wall reactions.

Uneven reflections of pressure waves due to wall geometry produce areas where pressure waves are more focused and superimposed, resulting in pressure oscillations. These radial mode-dominated oscillations push energy into a smaller and smaller volume as the pressure wave moves inward. A pressure wave rapidly compresses the gases at the wave-front before the gases have time to exchange heat outward, and this adiabatic compression produces a temperature rise based on the adiabatic process equation and reinforced by the interior ballistic code analyses. For adiabatic process equation calculations of typical propellant products, pressure is inversely proportional to density to the gamma (typically 1.223); a 2.0 fold increase in pressure gives a 1.8 fold increase in density and a 1.1 fold increase in temperature.

Position-dependent minimum pressure and temperature oscillations are due mainly to combustion and expansion, due less to adiabatic compression, and drop these positions below their flame temperatures. Position-dependent maximum pressure and temperature oscillations occur with very little liquid (or solid) and are dominated by adiabatic compression. The pressure oscillations at each position cause temperature oscillations up and down the indicated curves based on interior ballistic calculations and supported by adiabatic process equation calculations.

Figure 1 shows typical interior ballistic code-generated pressure oscillations and their resulting temperature oscillations for the SPT, SPH, and LPH generic gun systems. The SPT and SPH systems have very low pressure and temperature oscillations, and only their averages are plotted since their maximum, average, and minimum oscillations would superimpose on this plot. The LPH system has substantial pressure and temperature oscillations, and its maximum, average, and minimum oscillations are plotted. The three solid circles indicate the maximum pressures and temperatures without hydrogen-embrittling CFs.

Figure 2 shows typical Figure 1-derived minimum temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated atomic hydrogen concentrations [H] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, each system increases its [H] product slightly with the addition of lubricant. The three solid circles indicate the maximum temperatures and [H] without hydrogen embrittling CFs.

Figure 3 illustrates typical Figure 1-derived minimum temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated molecular hydrogen concentrations [H₂] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, the SPT,L, SPT, SPH,L, and SPH systems are grouped in a narrow range of [H₂] product values, the LPH system has very low [H₂] values, but the LPH,L system has enormous [H₂] values. Unfortunately for the LPH,L gun system, the significant lubricant required for the operation of firing each shot becomes a highly embrittling part of the combustion products. The three solid circles indicate the maximum temperatures and [H₂] without hydrogen-embrittling CFs.

Figure 4 illustrates typical Figure 1-derived average temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated atomic hydrogen concentrations [H] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, the SPT,L, SPT, SPH,L, and SPH systems increase [H] product values slightly with the addition of lubricant compared to the minimum oscillations shown in Figure 2. Also, for these oscillations, the LPH,L and LPH systems still have [H] values below the four other systems, but the addition

of lubricant and oscillations has given moderate increases compared to the minimum oscillation shown in Figure 2. The three solid circles indicate the maximum temperatures and [H] without hydrogen-embrittling CFs.

Figure 5 shows typical Figure 1-derived average temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated molecular hydrogen concentrations [H₂] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, the SPT,L, SPT, SPH,L, and SPH systems are grouped in a narrow range of [H₂] product values, the LPH system has very low [H₂] values, but the LPH,L system still has enormous [H₂] values, which very subtly increase from Figure 3. Unfortunately for the LPH,L gun system, the significant lubricant required for the operation of firing each shot continues to become a highly embrittling part of the combustion products. The three solid circles indicate the maximum temperatures and [H₂] without hydrogen-embrittling CFs.

Figure 6 shows typical Figure 1-derived maximum temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated atomic hydrogen concentrations [H] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, the SPT,L, SPT, SPH,L and SPH systems increase [H] product values slightly with the addition of lubricant compared to the minimum oscillations shown in Figure 2. Also, across the entire temperature range for these maximum oscillations, the LPH,L and LPH systems still have [H] values from below to equal the four other systems, but the addition of lubricant and oscillations has given significant increases compared to the minimum oscillation shown in Figure 2. The three solid circles indicate the maximum temperatures and [H] without hydrogen-embrittling CFs.

Figure 7 illustrates typical Figure 1-derived maximum temperature oscillations and their resulting nonideal gas-wall thermochemical code-generated molecular hydrogen concentrations [H₂] for the SPT,L, SPT, SPH,L, SPH, LPH,L, and LPH generic gun systems. For these oscillations, the SPT,L, SPT, SPH,L, and SPH systems are grouped in a narrow range of [H₂] product values, the LPH system has very low [H₂] values, but the LPH,L system still has enormous [H₂] values, which subtly continue to increase compared to Figures 3 and 5. Unfortunately for the LPH,L gun system, the significant lubricant required for the operation of firing each shot continues to become a highly embrittling part of the combustion products. The three solid circles indicate the maximum temperatures and [H₂] without hydrogen-embrittling CFs.

Since EAC, or more specifically HAC, has resurfaced in the last five years as a service life-limiting factor for some gun system designs, what role does HAC by chemical factors play in the generic gun systems examined? In these HAC-affected system designs, mechanical loading factors alone do not appear to explain this loss of service life; chemical factors are also implicated. This study indicates that HAC is the type of EAC responsible for such service life limitation.

These hydrogen-embrittling chemical factors include:

- A major effect due to the addition of lubricants
- A minor effect due to pressure oscillations
- A subtle effect due to gaseous water-wall reactions
- Another subtle effect due to wall material choice
- Nearly no effect due to gaseous acid-wall reactions

For the LPH,L generic gun system, the atomic hydrogen concentrations [H] in Figures 2, 4, and 6 are substantially affected by that system's variable pressure and temperature oscillations, but the resulting [H] product values range from equal to less than the SPT,L, SPT, SPH,L, and SPH generic gun systems placing [H] and oscillations as minor embrittling chemical factors. For the LPH,L generic gun system, the gaseous water effect ranges from equal to 30 percent higher than the SPT,L, SPT, SPH,L, and SPH generic gun systems placing the gaseous water-wall reactions as a subtle embrittling chemical effect. For all six generic gun systems, the wall material effect ranges from equal to within 20 percent of each of the other systems placing this as another subtle effect. For all six generic gun systems, the gaseous acid-wall reactions effect ranges from equal to within 10 percent of each of the other systems placing this as a near nonexistent effect.

There is a 35 to 40 percent [H₂] product increase in the SPH,L and SPT,L systems compared to their nonlubricated systems and this should not be ignored for that first shot after storage even though there has not been a major embrittling failure of late.

For the LPH,L generic gun system, the molecular hydrogen concentrations [H₂] in Figures 3, 5, and 7 are only subtly affected by that system's variable pressure and temperature oscillations due to the fact that [H₂] product is the largest mole fraction component unlike the other five system cases. The implication of gaseous molecular hydrogen in the LPH,L system explains why the use of a strong acid-type electrochemical cell that produces hydrogen gas at the cathodic wall material was successful at embrittling the wall material and a nitric acid cell was unsuccessful since it passivates the wall and produces little hydrogen. The lubricant-derived [H₂] product in the LPH,L system is its major embrittling chemical factor, where oscillations play only a minor role. It should be noted that this LPH,L case was for a high-zone shot and that the lubricant-to-propellant ratio increases as zone decreases, further increasing the molar portion of [H₂] product.

The LPH system has a stoichiometric propellant product (mostly water, nitrogen, and carbon dioxide in that order), but the LPH,L system has an embrittling hydrogen-rich and oxygen-deficient propellant-lubricant product combination (mostly molecular hydrogen, carbon monoxide, water, nitrogen, and carbon dioxide in that order). In fact, the LPH,L system has 3 to 7 times the

[H₂] product of the SPT,L, SPT, SPH,L, and SPH systems and 100 to 1000 times the [H₂] of the fictitious LPH system, which lacks lubricant. The hydrogen-embrittling effect of the lubricant in the LPH,L system would be enormously decreased if a stoichiometric propellant-lubricant product combination could be designed. This is not as easy as it sounds since the key is not simply to decrease the hydrogen richness, but to overcome the oxygen deficiency of the combined propellant-lubricant system. For example, it is not enough to replace the hydrocarbon lubricant with a nonhydrocarbon lubricant, since the nonhydrocarbon lubricant could still combine with the propellant's oxygen and provide a similar hydrogen-rich, oxygen-deficient combined system.

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Fig 1 - Resulting Temperatures Due To Pressure Oscillations

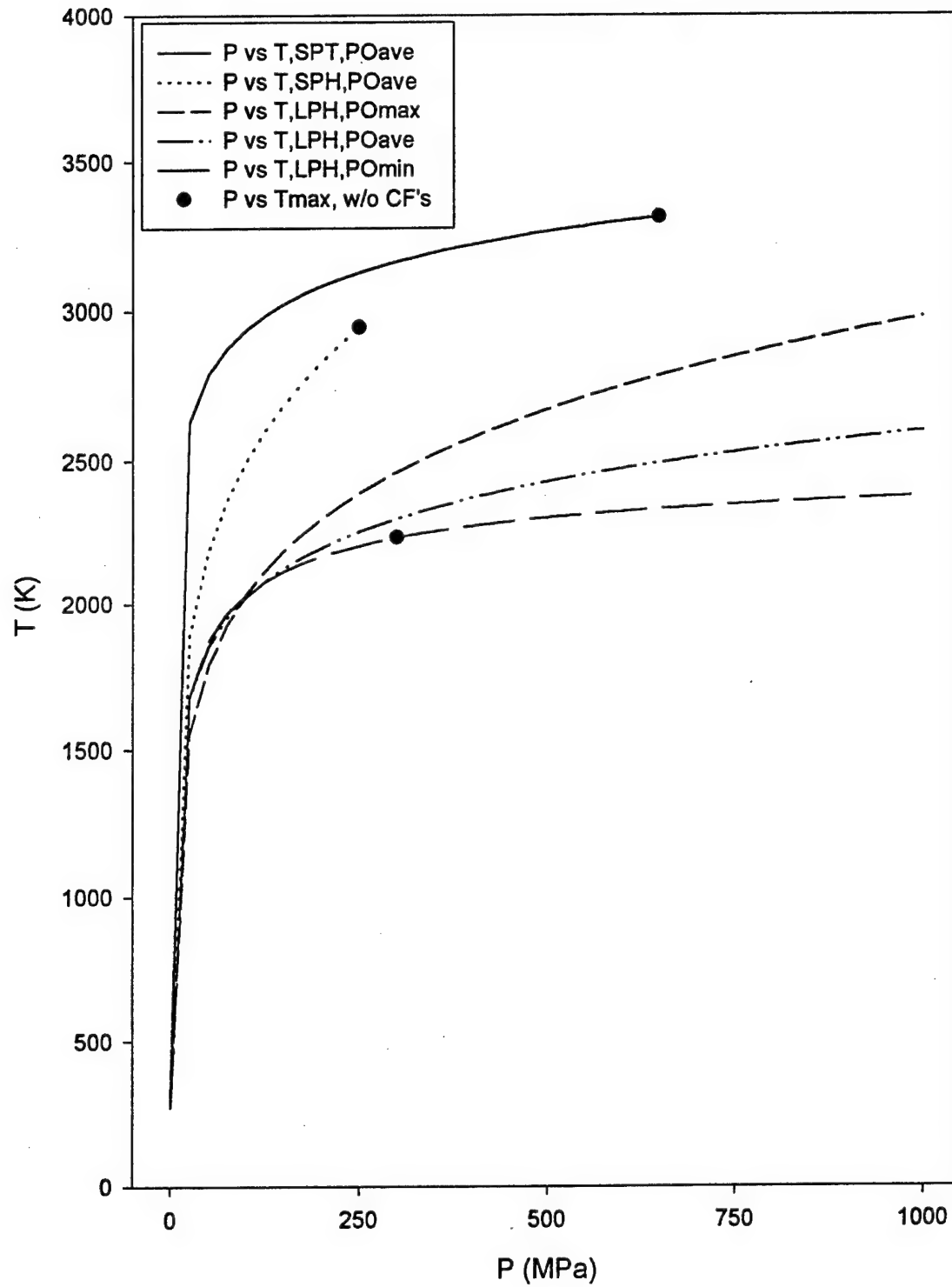


Fig 2 - Resulting [H] Due To Minimum Temperature Oscillations

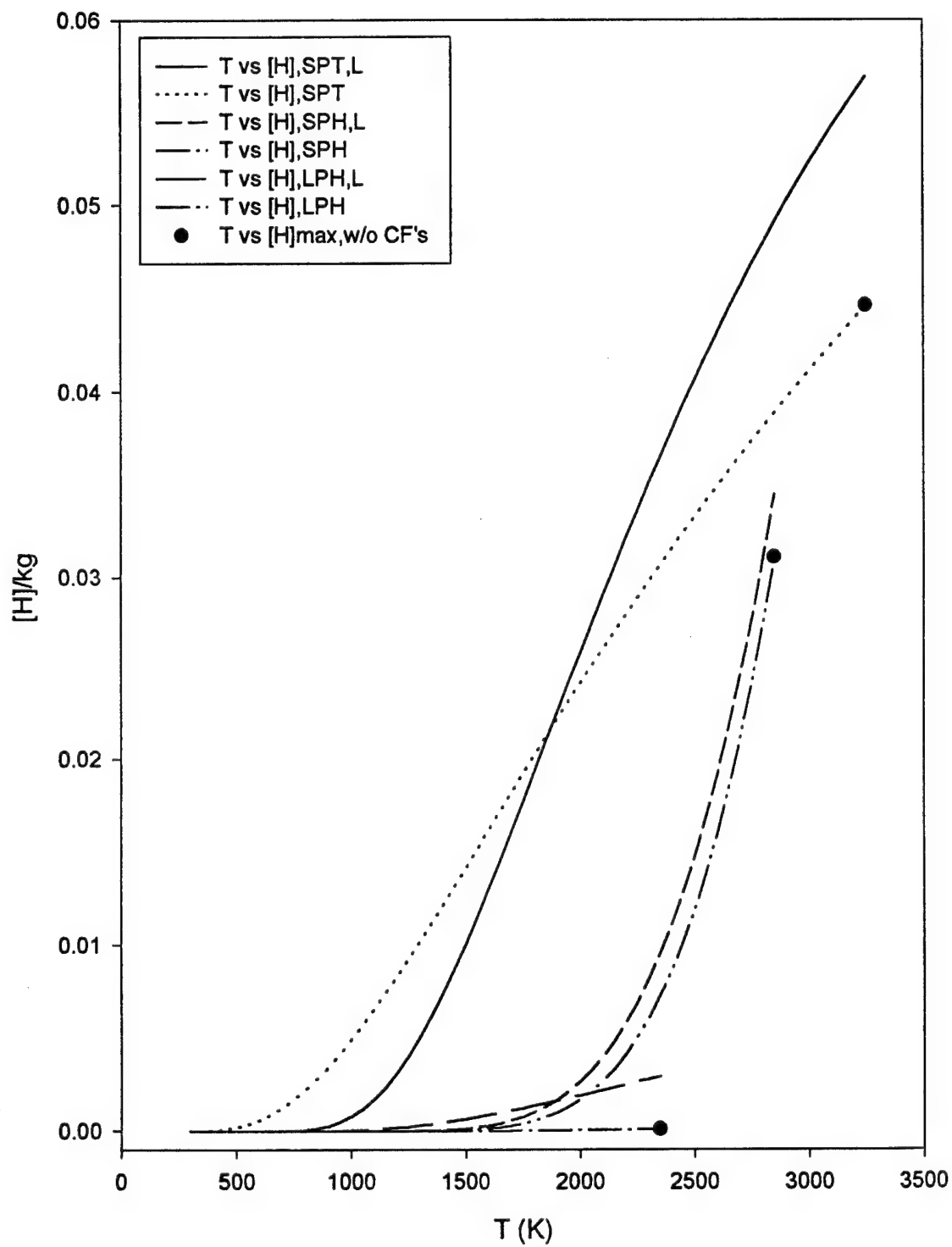


Fig 3 - Resulting [H2] Due To Minimum Temperature Oscillations

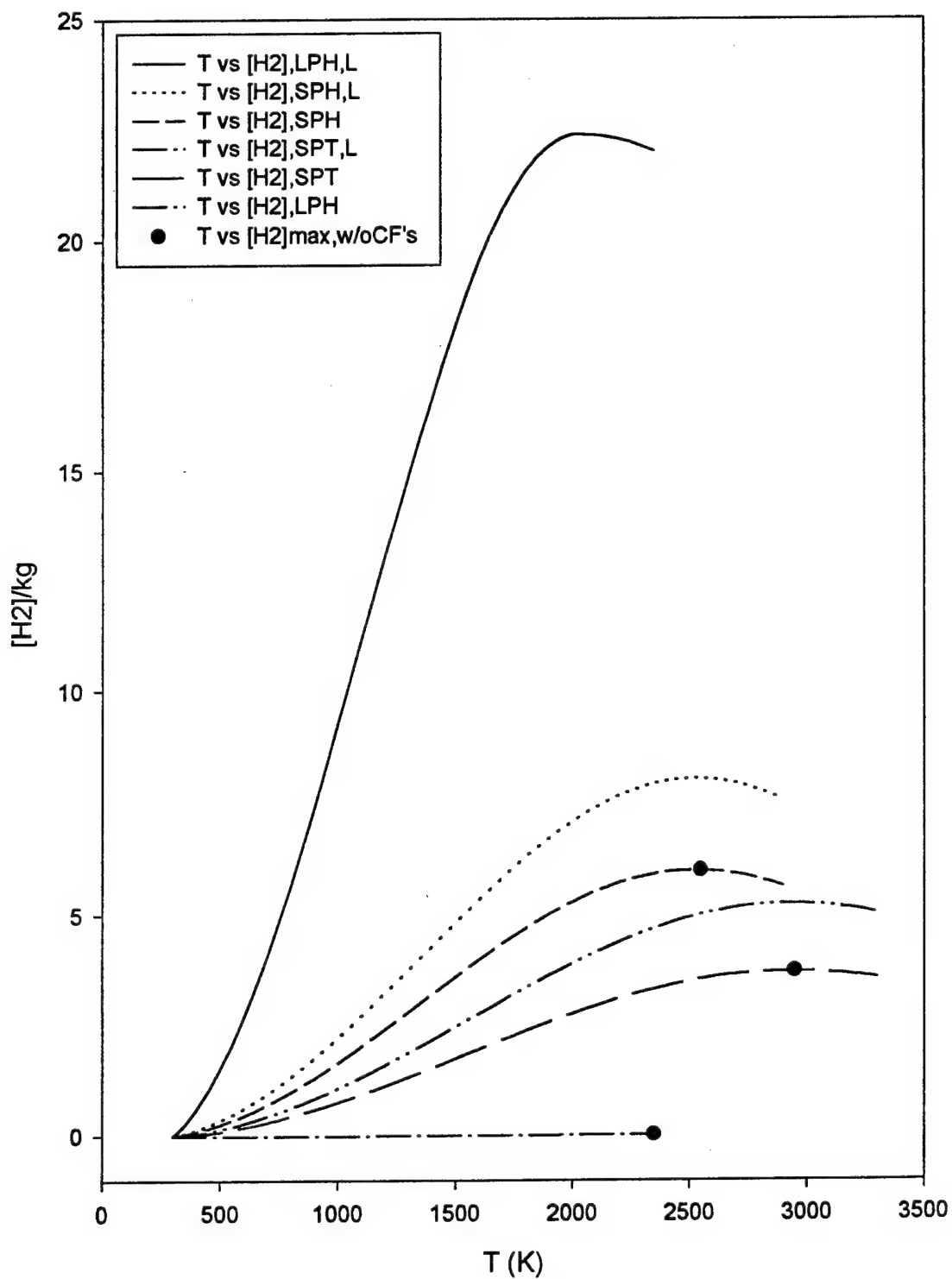


Fig 4 - Resulting [H] Due To Average Temperature Oscillations

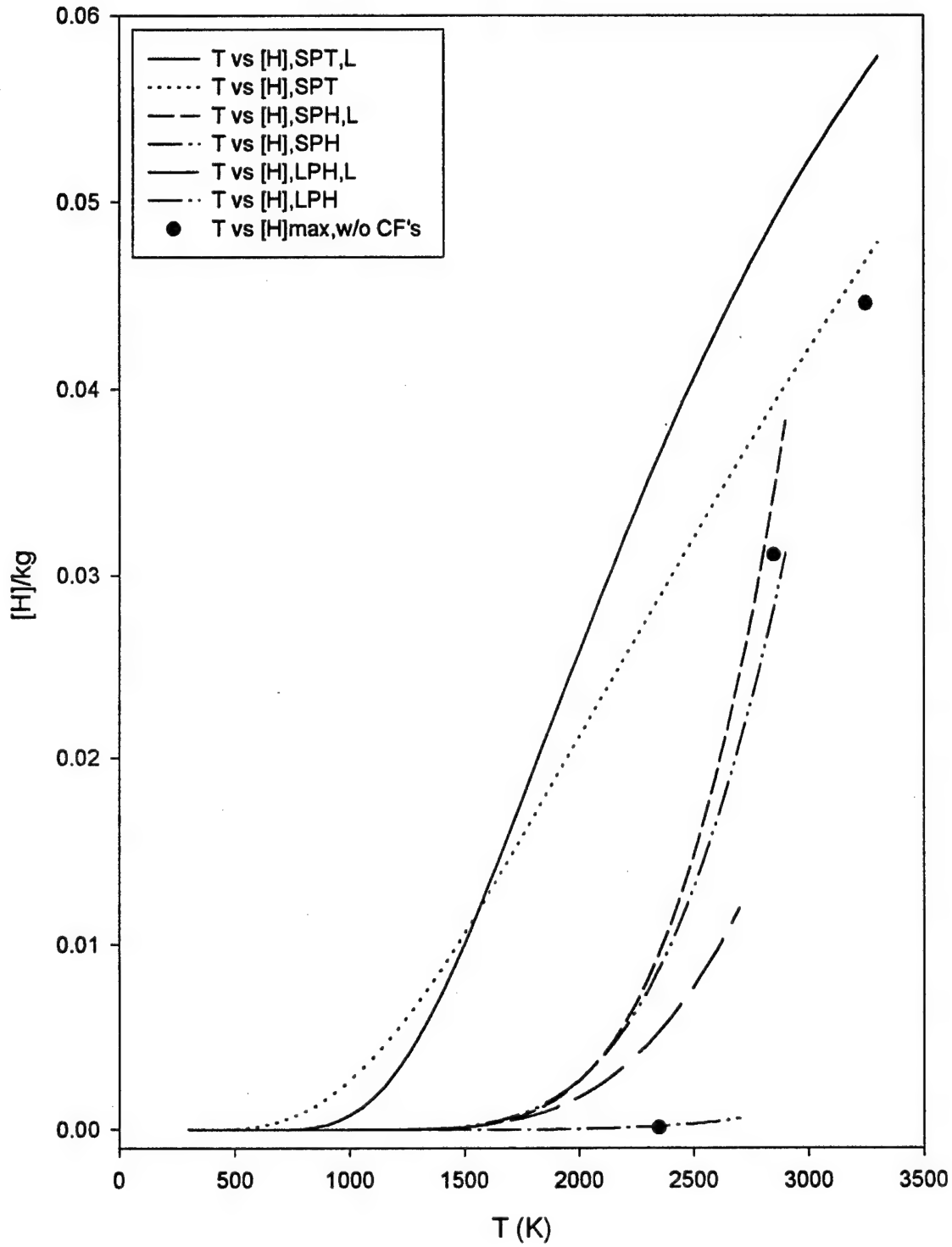


Fig 5 - Resulting [H2] Due To Average Temperature Oscillations

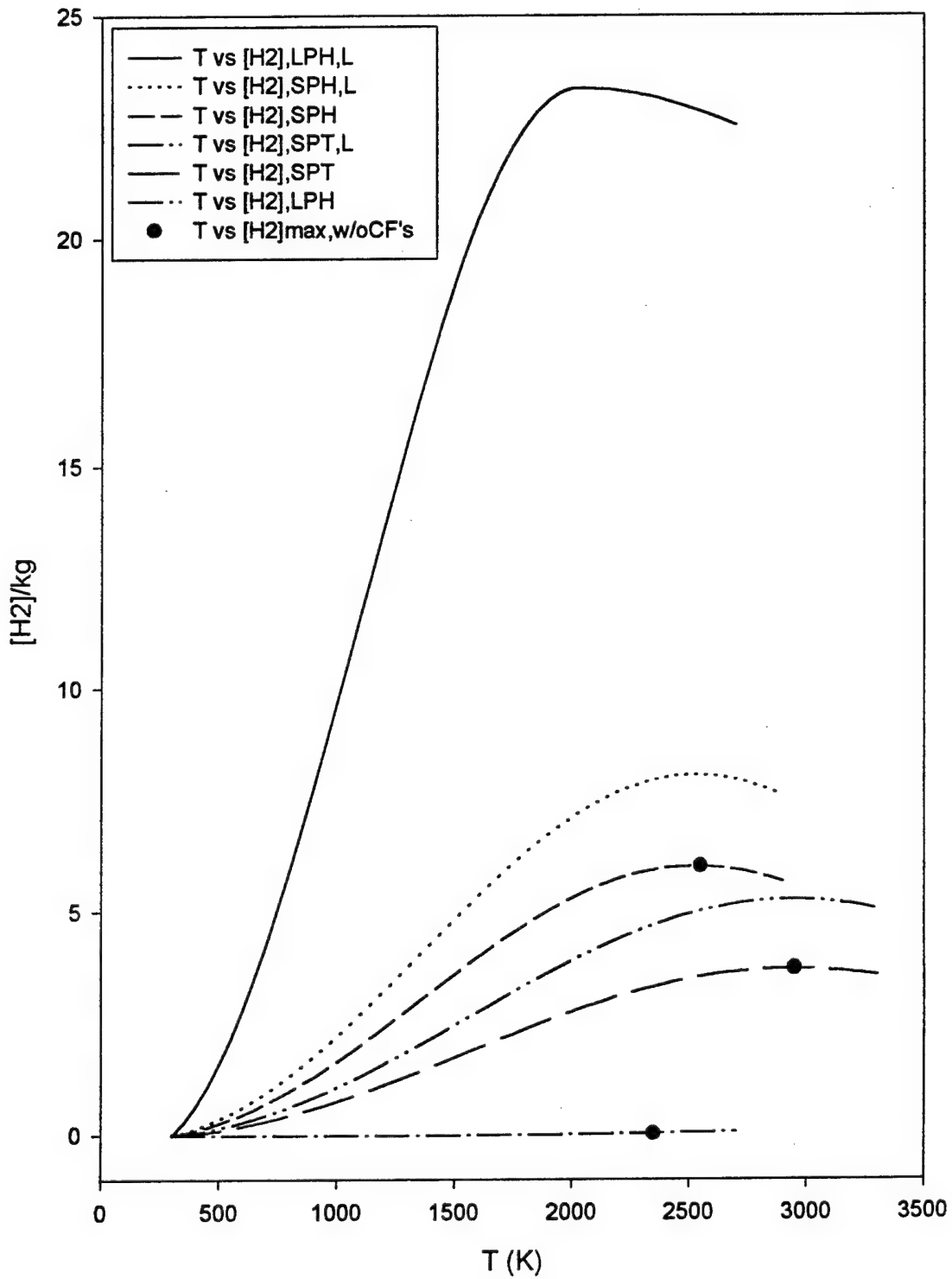


Fig 6 - Resulting [H] Due To Maximum Temperature Oscillations

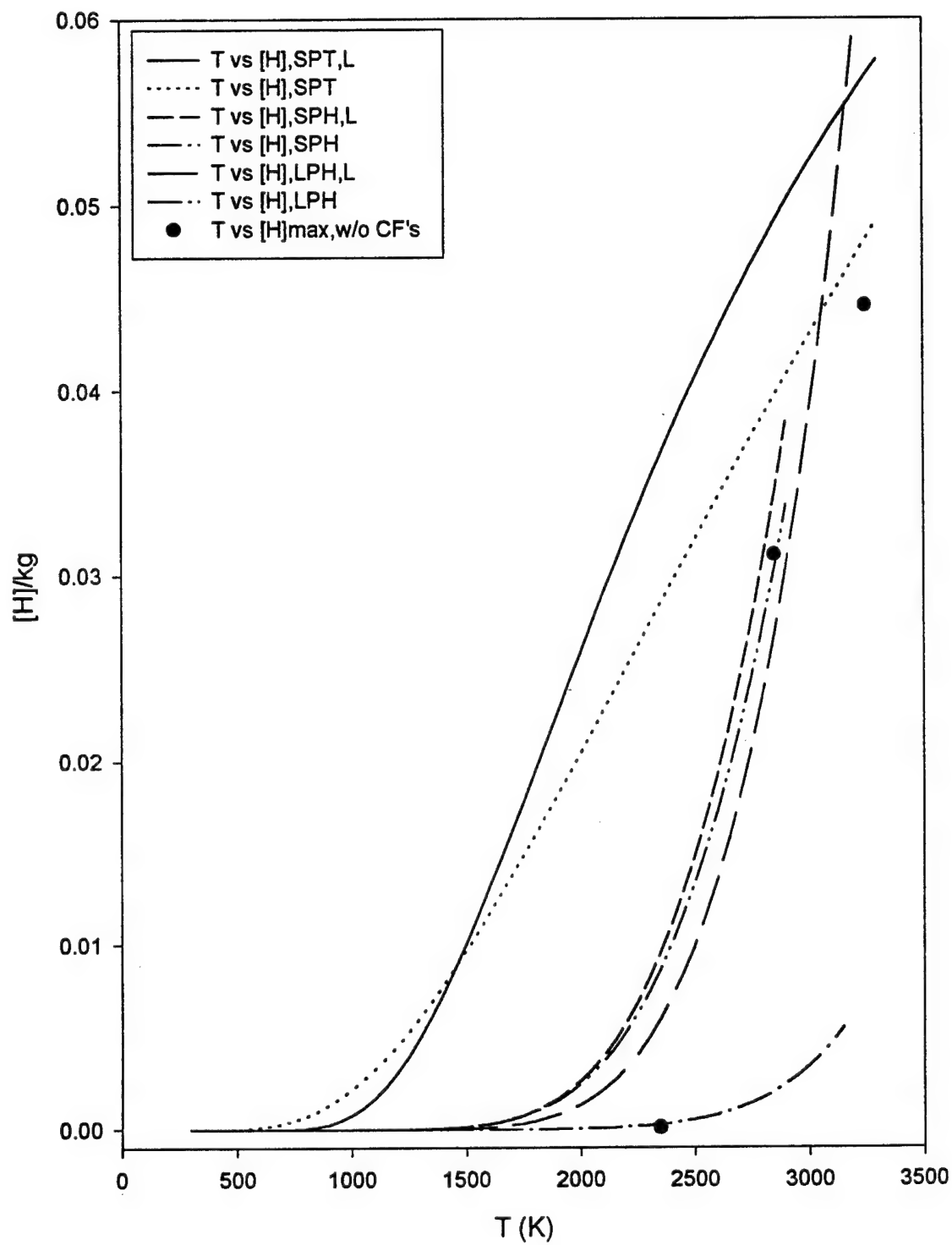
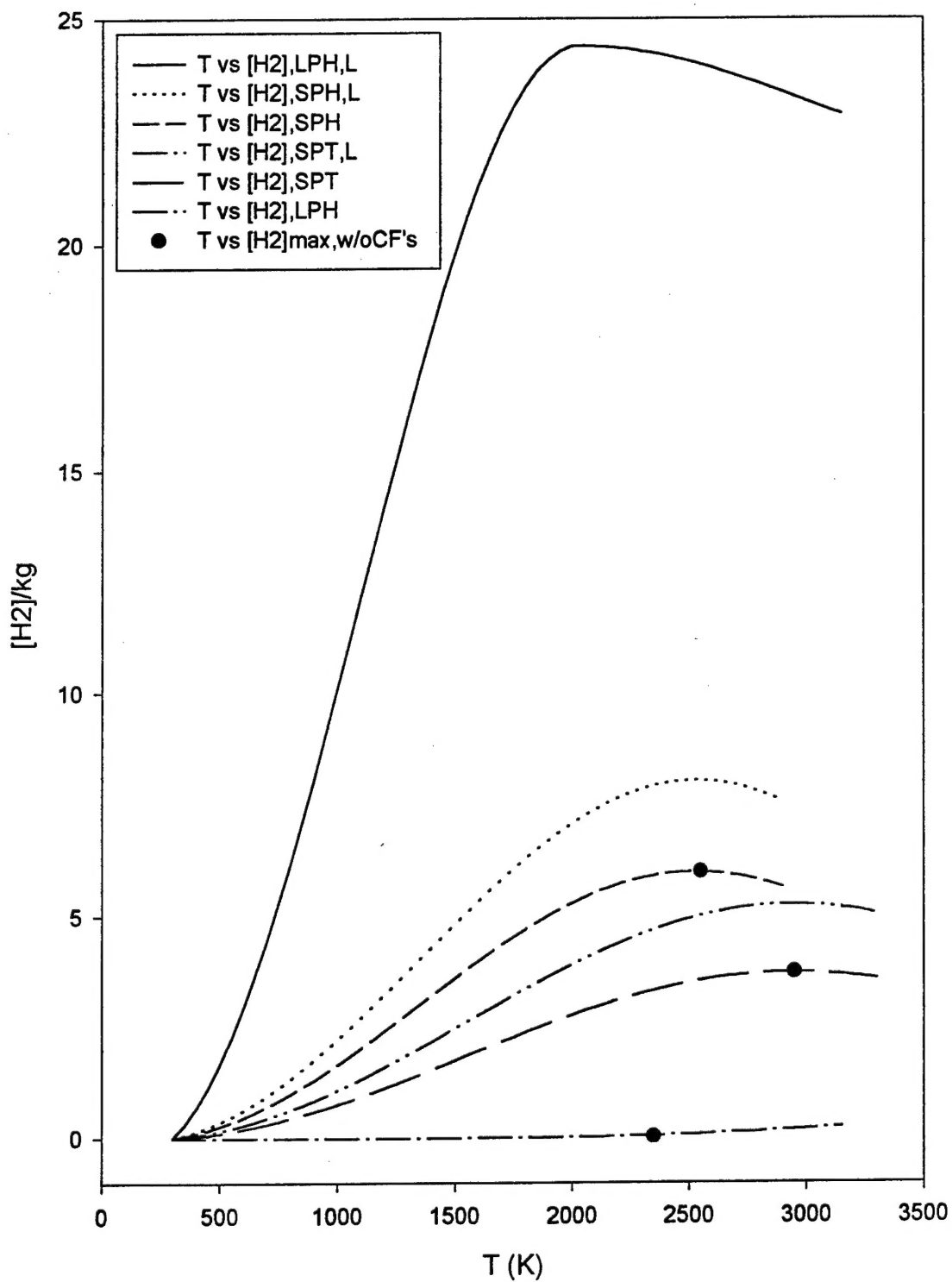


Fig 7 - Resulting [H2] Due To Maximum Temperature Oscillations



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